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(54) **Process for the preparation of a coating for forming a transparent and electrically conductive film and its use**

(57) A coating solution for forming a transparent and electrically conductive film contains fine conductive metal or alloy particles dispersed in a polar solvent and having a diameter not exceeding 50 nm. The metal particles

are of silver and at least one of palladium, copper and gold. The alloy particles are of an alloy of silver with at least one of palladium, copper and gold. The solution permits the use of a baking temperature which is as low as 150-450°C.

*Ag + (Pd, Cu, Au)*



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# EUROPEAN SEARCH REPORT

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## DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 514 557 A (CATALYSTS & CHEM IND CO) 25 November 1992 * page 5, line 19 - line 44 * * page 5, line 45 - page 6, line 31 * * page 6, line 45 - line 50 *	1-3	C09D5/24 H01B1/22 H01B1/20
A	DE 42 28 603 A (FRAUNHOFER GES FORSCHUNG) * claims 1-9 *	1	
A,D	PATENT ABSTRACTS OF JAPAN vol. 095, no. 001, 28 February 1995 & JP 06 279755 A (SUMITOMO METAL MINING CO LTD:OTHERS: 01), 4 October 1994, * abstract *	1	
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The present search report has been drawn up for all claims			

Place of search	Date of publication of the search	Examiner
THE HAGUE	23 January 1998	Miller, A
CATEGORY OF CITED DOCUMENTS		
<p>1. particularly relevant if taken alone</p> <p>2. particularly relevant if combined with another document of the same category</p> <p>3. relevant for background</p> <p>4. non-written document</p> <p>5. intermediate document</p> <p>6. closely connected underlying the invention</p> <p>7. earlier patent document and published on or after the filing date</p> <p>8. document cited in the application</p> <p>9. document cited for other reasons</p> <p>10. member of the same patent family (corresponding document)</p>		

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(54) **Process for the preparation of a coating for forming a transparent and electrically conductive film and its use**

(57) A coating solution for forming a transparent and electrically conductive film contains fine conductive metal or alloy particles dispersed in a polar solvent and having a diameter not exceeding 50 nm. The metal particles

are of silver and at least one of palladium, copper and gold. The alloy particles are of an alloy of silver with at least one of palladium, copper and gold. The solution permits the use of a baking temperature which is as low as 150-450°C.

**EP 0 803 551 A2**

## D scription

This invention relates to a coating solution for forming a transparent and electrically conductive film for imparting an electric-field shielding effect to the front glass of a cathode-ray tube, as of a display unit in an OA apparatus, or of a television receiver, a transparent and electrically conductive film formed therefrom and a process for forming the same. More particularly, it relates to a coating solution prepared by dispersing fine electrically conductive particles containing silver in a polar solvent, and used for forming a transparent and electrically conductive film having a higher level of electric conductivity than any similar film known in the art, and suited for shielding a low-frequency electric field.

The recent tendency toward office automation (OA) has brought about the introduction of so many OA apparatus into offices that it is not unusual for many people to work in an office all day facing the display unit of an OA apparatus. The cathode-ray tube (CRT) of a computer is required to have a clearly visible display screen which does not fatigue the eyes of anybody working close to it, and which is free from any dust adherence, or electric shock caused by the accumulation of charge on its surface. Moreover, it is nowadays feared that the low-frequency electromagnetic waves emitted by CRTs may have an adverse effect on the human body, and CRTs not leaking out any such waves are wanted.

The electromagnetic waves are emitted by deflecting coils and flyback transformers, and as television receivers become larger, electromagnetic waves of higher intensity tend to leak out. The leakage of a magnetic field can for the greater part be prevented by, for example, employing a differently shaped deflecting coil.

The leakage of an electric field can be prevented by forming an electrically conductive transparent film on the surface of the front glass of a CRT. This method is based on the same principle with the measure which has hitherto been taken to prevent the accumulation of charge. The electric conductivity of the film is, however, required to be by far higher than that of the film formed for preventing the accumulation of charge. While a film having a surface resistivity of, say,  $10^8 \Omega/\square$  is satisfactory for preventing the accumulation of charge, it is necessary to form a transparent film having a low resistivity not exceeding  $10^6 \Omega/\square$ , and preferably in the order of  $10^2$  to  $10^3 \Omega/\square$  for preventing the leakage of an electric field.

Several methods have hitherto been proposed to comply with the above requirements. According to one of them, a film of an electrically conductive oxide, such as tin or indium oxide, is formed on the surface of the front glass of a CRT by vacuum evaporation, CVD, sputtering, etc. The film formed by this method has a sufficiently low resistivity for shielding an electric field, since it is of a single material, such as tin or indium oxide, and retains the electric conductivity of its material. Moreover, the film can be formed with so small and uniform a thickness as not to affect the resolving power of the CRT, and

as to be easily treated against reflection.

The formation of the film, however, requires a large amount of cost obstructing the manufacture of practically useful CRTs, since it is necessary to prepare an appropriately controlled atmosphere for each individual CRT. Thus, these methods have been considered inadequate except for CRTs intended for special use, and there has been wanted a process for forming a film in a simpler process at a low cost.

A treating solution for forming an electric-field shielding film which is prepared by dispersing a very fine powder of indium tin oxide (ITO) and an alkyl silicate as a binder in a polar solvent consisting mainly of N-methyl-2-pyrrolidone has been proposed as being capable of realizing a low surface reactivity at a low cost (Japanese Laid-Open Patent Application No. Hei 6-279755). If the solution is applied onto the front glass of a CRT, dried, and baked at a temperature not exceeding  $200^\circ\text{C}$ , it is possible to form a film having a surface resistivity of  $10^3$  to  $10^5 \Omega/\square$ , depending on its thickness. The application of this ink is a highly beneficial method for the electric-field shielding of a CRT, since it is by far simpler and less expensive than the other methods of forming a transparent and electrically conductive film, such as vacuum evaporation and sputtering. There has, however, been a lower limit to the surface resistivity of the film which can be realized, and it has been difficult to achieve a desirable surface resistivity in the order of  $10^2$  to  $10^3 \Omega/\square$ .

The electrically conductive film is not allowed to impair the transparency or resolution of the screen, and it is also desirable that its transmittance be somewhat controllable. While the transmittance of the front glass of a CRT can be lowered to a certain level to achieve an improved image contrast, it lacks uniformity due to a difference in glass thickness between center and edges, and it is, therefore, desirable that the transmittance of the film formed thereon be adjustable by, say, 10 to 20%. In order to achieve a lower transmittance of light without lowering the resolution, while it is, of course, necessary to produce a uniformly darkened picture, it is desirable that the diffusive scattering of light by the film be minimized, and that its transmittance be lowered by means of the absorption of light by the material of the film.

The solution prepared by employing an ITO powder as described above, however, fails to realize the low transmittance of light having a dark color which is adjustable in brightness, since the powder essentially has the property of transmitting visible light. Thus, the film in which fine particles of ITO are dispersed has been unsatisfactory in electric conductivity and visible-light transmittance controllability.

It is an object of this invention to provide a coating solution for forming at a low cost by a simple method a transparent and electrically conductive film having the function of restraining the reflection of light on the surface of a CRT screen and the function of lowering its transmittance of visible light without scattering it, and

having a higher degree of electric conductivity than any known film to cut off a low-frequency electric field which may have an adverse effect on the human body, a transparent and electrically conductive film formed therefrom and a process for forming it.

The above object is attained by a coating solution comprising fine electrically conductive metal or alloy particles dispersed in a polar solvent and having a diameter not exceeding 50 nm, the metal particles being of silver (Ag) and one or more other metals selected from the group consisting of palladium (Pd), copper (Cu) and gold (Au), or the alloy particles being of a silver alloy formed from silver (Ag) and one or more other metals selected from the group consisting of palladium (Pd), copper (Cu) and gold (Au).

The solution may further contain one or more compounds selected from the group consisting of tin-containing indium oxide, antimony-containing tin oxide and aluminum-containing zinc oxide. The solution may further contain a partially hydrolyzed and polymerized alkyl silicate.

The above object is also attained by a transparent and electrically conductive film formed from any of the solutions as set forth above.

The above object is further attained by a process which comprises coating a base material with any of the solutions comprising metal or alloy particles as set forth above, and with a solution of a partially hydrolyzed and polymerized alkyl silicate, and baking it.

A transparent and electrically conductive film having an electric-field shielding effect can be formed easily at a low cost on the spherical surface of a complete CRT, or the surface of a front glass for a CRT before its sealing if the coating solution of this invention is applied onto the surface, dried, and baked in the air. The film has a single layer, and its strength can be increased by applying thereon a solution containing a partially hydrolyzed and polymerized alkyl silicate. Its baking may be carried out at a temperature of, say, 150-450°C.

The fine electrically conductive particles which are employed for the purpose of this invention consist mainly of silver (Ag), and further contain one or more other metals selected from the group consisting of palladium (Pd), copper (Cu) and gold (Au). The other metal (or metals) may be in the form of films or fine particles covering fine silver particles, or may form an alloy with silver, or may exist as a mixture of those two forms. The metal (or metals) other than silver may be used in the amount of 0.1 to 30% by weight, since less than 0.1% by weight results in a film lacking stability in resistivity, while over 30% by weight results in a film having a high resistivity.

The fine electrically conductive particles have a specific resistivity in the order of  $10^{-5}$  to  $10^{-6} \Omega \text{cm}$ , which is two or three orders lower than that of a transparent and electrically conductive oxide, such as tin-containing indium oxide (ITO), antimony-containing tin oxide (ATO) or aluminum-containing zinc oxide (AZO). The particles form conductive pathes in a film as a result of mutual

contact and enable it to realize a resistivity which is lower than that of a film formed from e.g. ITO particles.

Such high conductivity can be expected when a coating solution contains at least 1% by weight of such particles. While a solution containing a larger amount of particles can form a conductive layer having a larger thickness and a lower surface resistivity, no solution containing over 10% by weight of particles is recommendable, since it is difficult to form a film having a smooth interfacial surface and the particles lower their dispersion stability in the solution and form a sediment which is not negligible. It is sufficient to use a solution containing less than, say, 7% by weight of particles in order to form a film having a surface resistivity in the order of  $10^2$  to  $10^3 \Omega/\square$ .

The solution may further contain fine transparent and electrically conductive oxide particles, such as ITO, ATO or AZO particles. These oxide particles serve to form a film having an improved transmittance, though it may have a somewhat higher resistivity. For any application not calling for a great reduction in brightness, it may be sufficient to use a solution consisting mainly of e.g. ITO, ATO or AZO, and containing a small amount of metal or alloy particles.

If the particles have too large a diameter, or are too cohesive, there is formed a hazy film which undesirably lowers the resolution of a CRT display. In order not to lower the resolution of a CRT display, it is usually necessary for a film to be sufficiently clear to have a haze not exceeding 5% as a value indicating the percentage of the amount of scattered transmitted light to the total amount of transmitted light.

The haze of a film is substantially proportional to its thickness, and as a result of the use of particles having different diameters, it has been found that a smaller diameter is preferable, and that it is important to use particles having an average diameter not exceeding about 50 nm in order to form a film having a thickness of, say, 0.1  $\mu\text{m}$  and a haze not exceeding 5%. If a film is formed from particles having an average diameter not exceeding 50 nm, the mode in which it scatters incident visible light is, in almost all the cases, of Rayleigh or Mie scattering, and hardly any scattering is due to the shape of the object. On the other hand, a film formed from particles having an average diameter exceeding 50 nm has a haze exceeding 5% easily, since an increased amount of light is scattered by the particles, or the film surface having a higher degree of coarseness.

The film formed from the solution of this invention preferably has a thickness of, say, 0.05 to 0.6  $\mu\text{m}$ . A film having a thickness not exceeding 0.6  $\mu\text{m}$  has a haze exceeding 5%. A uniform film having a thickness which is smaller than 0.05  $\mu\text{m}$  is difficult to form by a process employing an ink. Experiments teach that a film having too small a thickness has an insular particle distribution which increases its surface unevenness and thereby its haze, as well as bringing about a sharp rise in resistivity.

All kinds of electrically conductive particles having

a very small diameter as stated above are relatively easy to manufacture, except ITO particles. ITO particles having an average diameter not exceeding 50 nm are generally difficult to manufacture, but are sold and supplied by Sumitomo Metal Mining Co., Ltd.

The coating solution of this invention can be prepared by dispersing fine electrically conductive particles having an average diameter not exceeding 50 nm in a polar solvent to form a highly concentrated dispersion, and mixing it with a polar solvent to dilute it. The dispersion of the particles is preferably carried out by mixing them in the polar solvent in a powerful dispersing machine and deflocculating the majority of flocculent particles into primary particles in a monodisperse state. A ball mill, or attritor sand mill can, for example, be used as the dispersing machine.

The polar solvent which can be used for dispersing the particles is of the type which has an appropriate boiling point not exceeding the baking temperature and can disperse the particles efficiently. Examples are water, N-methyl-2-pyrrolidone (NMP), ethanol, 4-hydroxy 4-methyl-2-pentanone (diacetone alcohol), isopropyl alcohol, N, N-dimethylformamide (DMF), diacetamide, methyl cellosolve, acetone and tetrahydroxyfuran. A small amount of e.g. a silane, titanate, zirconate or aluminate coupling agent, or a polycarboxylic acid, phosphoric ester, or silicone surface active agent can be added as a dispersant for raising the dispersibility of the particles. The dispersant can be added in a small amount not exceeding 1% by weight unless it affects electric conductivity.

The polar solvent used for the diluting purpose is selected from among the solvents which are compatible with the solvent used for the dispersing purpose and also with the dispersant, and have a boiling point not exceeding the baking temperature. The polar solvent for the diluting purpose is employed for improving the applicability of the solution to a base to enable it to form a smooth and uniform film. It will be easy for anybody of ordinary skill in the art to select a suitable solvent.

The partially hydrolyzed and polymerized alkyl silicate is used for bonding and fixing the particles to a glass surface. It is possible to use, for example, an orthoalkyl silicate which has been hydrolyzed and somewhat polycondensed with dehydration. Examples of orthoalkyl silicates are orthomethyl silicate,  $\text{Si}(\text{OCH}_3)_4$ ; orthoethyl silicate,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ; orthopropyl silicate,  $\text{Si}(\text{OC}_3\text{H}_7)_4$ ; and orthobutyl silicate,  $\text{Si}(\text{OC}_4\text{H}_9)_4$ . It is also possible to use an ortho-alkyl silicate having two or more alkyl groups in the same molecule, or a mixture of two or more alkyl orthosilicates.

The orthoalkyl silicates are easily hydrolyzed in the presence of water to have their alkoxy groups converted to hydroxyl groups, and undergo polycondensation with the liberation of water from the hydroxyl groups. A somewhat polymerized product can be used for the purpose of this invention. In short, it is possible to use an orthoalkyl silicate which undergoes polycondensation

with dehydration under heat and eventually forms a silica gel, or silica to fix fine electrically conductive particles to a glass surface. Its polycondensation can be promoted in the presence of a small amount of water, or an acid such as hydrochloric or sulfuric acid, as a reaction accelerator.

Although the partially hydrolyzed and polymerized alkyl silicate can be prepared from an orthoalkyl silicate as described above, its starting material is not necessarily limited to an orthoalkyl silicate if a similar product can be obtained. For example, Ethyl Silicate 40 and Methyl Silicate 51 (Tama Chemical Industrial Co., Ltd.) are commercially available, and these compounds can be used as they are, or after further hydrolysis and polycondensation, and appropriate dilution. It is also possible to add a hydrolyzed product of alkoxide, such as titanium, zirconium or aluminum, if necessary.

It is desirable that the above alkyl silicate be added in an amount not exceeding that of the conductive particles in terms of  $\text{SiO}_2$  as solidified, or that no such silicate be added. Therefore, it is desirable to limit its amount to 10% by weight at maximum, since the amount of the particles in the solution is preferably from 0.1 to 10% by weight. If the solution contains a larger amount of such silicate, it forms a film having a high haze and high resistivity due to the roughening of its interfacial surface or the worsening of the packing density of conductive particles. Although the addition of the alkyl silicate may be useful for improving the applicability of the solution to a base and the adhesion of a film to it, it is not necessary to add it to a solution for forming a first layer in the event that overcoating is done to form a two-layer film having a satisfactorily high surface strength.

After its application onto the face panel of a CRT, the coating solution of this invention is baked at a temperature of 150-450°C in the air. It is possible to heat it to a temperature immediately below the softening point of glass to form a film on the front glass of a CRT before its vacuum sealing, but in the event that a film is formed on the spherical surface of a complete CRT after its sealing, it is advisable to employ a heating temperature not exceeding 200°C, since a higher temperature is likely to cause its bursting.

The baking of the solution causes the polycondensation of the silicate, the evaporation of the solvent and the shrinkage, drying and hardening of the film as formed. As the polycondensation of the silicate is completed at a temperature of 200°C to 250°C, a small amount of ink components unavoidably remain unreacted and unevaporated at a baking temperature not exceeding 200°C. Therefore, it is generally advisable to use a higher temperature if possible, though a considerably strong film can be formed even at a baking temperature not exceeding 200°C. If a baking temperature of 250°C or above is used, the gel condensation of the silicate and its drying are completed, and the resulting shrinkage of the film allows it to have a higher packing density of conductive particles and a lower surface re-

sistivity. The mutual contacts of the conductive particles are improved with the evaporation of the solvent and improve the stability of the film in resistivity against any change with time.

The coating solution of this invention is a dispersion of fine electrically conductive particles, and is not intended for forming a film of those particles by relying upon the decomposition or chemical reaction of its components by the heat applied for baking. Therefore, it can form a film which is stable in properties and uniform in thickness. Moreover, it enables the formation of such a film at a low temperature as stated above, since it is sufficient to use a baking temperature which promotes the evaporation of the solvent and the dispersant and the polymerization and solidification of the alkyl silicate.

The following is a description of examples in which this invention is embodied. The solution containing a partially hydrolyzed and polymerized alkyl silicate (hereinafter referred to as "silicate solution") which was employed in the following examples had been prepared by mixing 30 parts of Ethyl Silicate 40 manufactured by Tama Chemical Industrial Co., Ltd. and having an average polymerization degree of 4 or 5 and 44 parts of ethanol, and dropping a solution of water and ethanol (46 parts of distilled water + 20 parts of ethanol) into their mixture under stirring, and further dropping a mixed solution composed of 10 parts of a 1% by weight aqueous solution for HCl and 7 parts of ethanol. It was appropriately diluted with a solvent, such as ethanol, prior to use. It is, however, to be understood that the silicate solution as described above is merely illustrative, and is not intended for limiting the scope of this invention.

The surface resistivity of each film was measured by employing a surface resistivity meter, MCP-T200, made by Mitsubishi Petrochemical Co., Ltd. Its haze and light transmittance were measured by employing a haze meter, HR-200, made by Murakami Color Technology Research Laboratory. Its reflectance was measured by employing a spectrophotometer made by Shimadzu Seisakusho after painting the rear surface of sheet glass black to restrain its reflection of light. The diameters of fine electrically conductive particles were measured by employing a transmission electron microscope made by JEOL.

#### Example 1

A coating solution, or dispersion containing 2% by weight of fine Ag-Pd particles was prepared by mixing under stirring 15 parts of ultrafine Ag-Pd particles made by Sumitomo Metal Mining Co., Ltd. and having an average diameter of 45 nm (containing 7% by weight of Pd, as determined by chemical analysis), 20 parts of dimethylformamide (DMF) and 5 parts of a silane coupling agent (TSL8802 made by Toshiba Silicone Co., Ltd.) as a dispersant, subjecting the mixture to 100 hours of dispersing action in a ball mill containing zirconia balls having a diameter of 5 mm. and mixing it with

ethanol strongly under stirring.

The coating solution was dropped from a beaker onto a sheet of soda-lime glass measuring 200 by 200 by 3 mm and rotating at a speed of 150 rpm. and was baked in the air at a temperature of 180°C for 30 minutes to form a single-layer film of dispersed Ag-Pd particles. The film had a surface resistivity of  $4.4 \times 10^3 \Omega/\square$ , a haze of 2.3% and a transmittance of 65%.

#### Example 2

The same coating solution as used in Example 1 was dropped from a beaker onto a sheet of soda-lime glass measuring 200 by 200 by 3 mm and rotating at a speed of 150 rpm, then the silicate solution as described above was dropped onto it, and the solutions were baked in the air at a temperature of 180°C for 30 minutes to form a two-layer film consisting of a dispersed Ag-Pd layer and an overcoat layer. The film had a surface resistivity of  $8.3 \times 10^2 \Omega/\square$ , a haze of 1.6% and a transmittance of 68%.

#### Example 3

A coating solution was prepared by using a titanate coupling agent (PRENACT KR138S made by Ajinomoto Corporation) as the dispersant and otherwise repeating Example 1, and a two-layer film was formed by repeating Example 2. The film had a surface resistivity of  $4.6 \times 10^3 \Omega/\square$ , a haze of 1.5% and a transmittance of 72%.

#### Example 4

A coating solution was prepared by repeating Example 1, and was thoroughly mixed under stirring with the silicate solution in a weight ratio of 95:5, and Examples 1 and 2 were repeated for the spin forming of a film on a sheet-glass base and its baking at 180°C to form a single-layer film and a two-layer film, respectively. The single-layer film had a surface resistivity of  $6.3 \times 10^4 \Omega/\square$ , a haze of 2.2% and a transmittance of 65% and the two-layer film had a surface resistivity of  $4.5 \times 10^3 \Omega/\square$ , a haze of 1.4% and a transmittance of 68%.

#### Example 5

A two-layer film was formed by employing a baking temperature of 400°C for 30 minutes and otherwise repeating Example 2. The film had a very high level of electric conductivity, as it had a surface resistivity of  $6.2 \times 10^2 \Omega/\square$ , a haze of 0.9% and a transmittance of 69%.

#### Example 6

A two-layer film was formed by employing ultrafine Ag-Au particles having an average diameter of 34 nm (containing 3.1% by weight of Au, as determined by chemical analysis) and otherwise repeating Example 2.

The film had a surface resistivity of  $8.7 \times 10^2 \Omega/\square$ , a haze of 1.6% and a transmittance of 73%, and was substantially equal in properties to the film formed from the Ag-Pd particles.

#### Example 7

A two-layer film was formed by employing ultrafine Ag-Cu particles having an average diameter of 41 nm (containing 4.5% by weight of Cu, as determined by chemical analysis) and a baking temperature of 350°C for 30 minutes and otherwise repeating Example 2. The film had a surface resistivity of  $1.7 \times 10^3 \Omega/\square$ , a haze of 1.4% and a transmittance of 71% and was substantially equal in properties to the film formed from the Ag-Pd particles.

#### Example 8

A two-layer film was formed by employing in a weight ratio of 3:1 the same ultrafine Ag-Pd particles having an average diameter of 45 nm as used in Example 1, and ultrafine ITO particles (ITO-UFP) made by Sumitomo Metal Mining Co., Ltd. and having an average diameter of 25 nm and otherwise repeating Example 2. The film had a surface resistivity of  $7.6 \times 10^3 \Omega/\square$ , a haze of 3.3% and a transmittance of 77%, and was improved in transmittance over the film formed from the Ag-Pd particles alone, though its surface resistivity was somewhat higher.

#### Example 9

A two-layer film was formed by employing in a weight ratio of 3:1 the same ultrafine Ag-Pd particles having an average diameter of 45 nm as used in Example 1, and ultrafine ATO particles made by Sumitomo Metal Mining Co., Ltd. and having an average diameter of 12 nm and otherwise repeating Example 2. The film had a surface resistivity of  $4.7 \times 10^4 \Omega/\square$ , a haze of 3.1% and a transmittance of 78%, and was improved in transmittance over the film formed from the Ag-Pd particles alone, though its surface resistivity was somewhat higher.

#### Example 10

A two-layer film was formed by employing in a weight ratio of 3:1 the same ultrafine Ag-Pd particles having an average diameter of 45 nm as used in Example 1, and ultrafine AZO particles made by Sumitomo Metal Mining Co., Ltd. and having an average diameter of 46 nm and otherwise repeating Example 2. The film had a surface resistivity of  $5.3 \times 10^4 \Omega/\square$ , a haze of 4.1% and a transmittance of 76%, and was improved in transmittance over the film formed from the Ag-Pd particles alone, though its surface resistivity was somewhat higher.

#### Example 11

A coating solution was prepared by mixing under stirring 10 parts of ultrafine Ag-Pd-Cu particles having an average diameter of 35 nm (and containing 2.5% by weight of Pd and 1.8% by weight of Cu as determined by chemical analysis), 30 parts of dimethylacetamide and 4 parts of a silane coupling agent (TSL8802 of Toshiba Silicone Co., Ltd.) as the dispersant and otherwise repeating Example 1. The solution contained 2% by weight of Ag-Pd-Cu particles. A two-layer film was formed from the solution by repeating Example 2. The film had a surface resistivity of  $1.4 \times 10^3 \Omega/\square$ , a haze of 1.6% and a transmittance of 72%, and was substantially equal in properties to the film formed from the Ag-Pd, Ag-Au or Ag-Cu particles.

#### Comparative Example 1

A two-layer film was formed by employing only ultrafine ITO particles (ITO-UFP) made by Sumitomo Metal Mining Co., Ltd. and having an average diameter of 19 nm without using any particles containing silver as set forth in claim 1, and otherwise repeating Example 2. The film had a surface resistivity of  $8.6 \times 10^3 \Omega/\square$ , but was not a dark one, as it had a transmittance of 96%.

#### Comparative Example 2

A film was formed by employing a highly conductive carbon powder made by Mitsubishi Chemical Co., Ltd. and having an average particle diameter of 8 nm and otherwise repeating Example 2. It had a transmittance of 46% and was a considerably dark film, and its surface resistivity was as high as  $3.9 \times 10^8 \Omega/\square$ .

As is obvious from the comparison of the foregoing Examples and Comparative Examples, the coating solution of this invention which is prepared by dispersing fine electrically conductive particles containing silver and one or more other metals selected from the group consisting of palladium, copper and gold can form a film having an appropriately low transmittance of light and yet a low haze, and a sufficiently high level of electric conductivity for shielding an electric field, while it is impossible to form a film having the desired properties including surface resistivity, transmittance and reflectance from any solution containing only a transparent and electrically conductive oxide, such as ITO, or a black conductor, such as carbon.

The coating solution of this invention can form a film having both good optical properties and high conductivity in a large quantity and at a low cost even at a baking temperature not exceeding 450°C, and including as low as 150°C, as stated above. The film can be formed on, for example, the surface of the screen of a CRT to provide an effective electric shield for preventing any trouble that might otherwise be caused by the leakage of electromagnetic radiation. Moreover, it enables the CRT



to provide a clear display with a low haze. Thus, this invention has a very high level of industrial utility.

#### Claims

1. A coating solution for forming a transparent and electrically conductive film which contains fine metal particles as fine conductive particles dispersed in a polar solvent, said metal particles comprising silver (Ag) and at least one other metal selected from the group consisting of palladium (Pd), copper (Cu) and gold (Au), and having a diameter of 50 nm at maximum. 5
2. A coating solution as set forth in claim 1, wherein said conductive particles further contain at least one compound selected from the group consisting of tin-containing indium oxide, antimony-containing tin oxide and aluminum-containing zinc oxide. 10
3. A coating solution as set forth in claim 1 or 2, further containing a partially hydrolyzed and polymerized alkyl silicate. 15
4. A coating solution as set forth in claim 1 or 2, containing 0.1 to 30% by weight of said other metal. 20
5. A coating solution as set forth in claim 1 or 2, containing 1 to 10% by weight of said conductive particles. 25
6. A coating solution as set forth in claim 1 or 2, wherein said conductive particles have a specific resistance in the order of  $10^{-5}$  to  $10^{-6} \Omega\text{-cm}$ . 30
7. A coating solution as set forth in claim 1 or 2, wherein said conductive particles have an average diameter of 50 nm at maximum. 35
8. A coating solution as set forth in claim 3, containing 0.1 to 10% by weight of said silicate. 40
9. A coating solution for forming a transparent and electrically conductive film which contains fine alloy particles as fine conductive particles dispersed in a polar solvent, said alloy particles being of a silver alloy formed by adding to silver (Ag) at least one other metal selected from the group consisting of palladium (Pd), copper (Cu) and gold (Au), and having a diameter of 50 nm at maximum. 45
10. A coating solution as set forth in claim 9, wherein said conductive particles further contain at least one compound selected from the group consisting of tin-containing indium oxide, antimony-containing tin oxide and aluminum-containing zinc oxide. 50
11. A coating solution as set forth in claim 9 or 10, further containing a partially hydrolyzed and polymerized alkyl silicate. 55
12. A coating solution as set forth in claim 9 or 10, containing 0.1 to 30% by weight of said other metal.
13. A coating solution as set forth in claim 9 or 10, containing 1 to 10% by weight of said conductive particles.
14. A coating solution as set forth in claim 9 or 10, wherein said conductive particles have an average diameter of 50 nm at maximum.
15. A coating solution as set forth in claim 11, containing 0.1 to 10% by weight of said alkyl silicate.
16. A transparent and electrically conductive film formed by employing a coating solution as set forth in claim 1 or 9.
17. A film as set forth in claim 16, having a thickness of 0.05 to 0.6  $\mu\text{m}$ .
18. A process for forming a transparent and electrically conductive film which comprises coating a base with a coating solution as set forth in claim 1 or 9, and further with a solution of a partially hydrolyzed and polymerized alkyl silicate, and baking said solutions.
19. A process as set forth in claim 18, wherein said baking is carried out at a temperature of 150°C to 450°C.

(19)



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(54) **Process for the preparation of a coating for forming a transparent and electrically conductive film and its use**

(57) A coating solution for forming a transparent and electrically conductive film contains fine conductive metal or alloy particles dispersed in a polar solvent and having a diameter not exceeding 50 nm. The metal particles

are of silver and at least one of palladium, copper and gold. The alloy particles are of an alloy of silver with at least one of palladium, copper and gold. The solution permits the use of a baking temperature which is as low as 150-450°C.



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# EUROPEAN SEARCH REPORT

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The present search report has been drawn up for all claims			
Place of search		Date of presentation of the search	Examiner
THE HAGUE		23 January 1998	Miller, A
CATEGORY OF CITED DOCUMENTS			
<p>1. particularly relevant if taken alone</p> <p>2. particularly relevant if combined with another document of the same category</p> <p>3. technological background</p> <p>4. non-written disclosure</p> <p>5. intermediate document</p> <p>6. already disclosed &amp; underlying the invention</p> <p>7. earlier patent document, but published on or after the filing date</p> <p>8. document cited in the application</p> <p>9. document cited for other reasons</p> <p>10. member of the same patent family (corresponding document)</p>			

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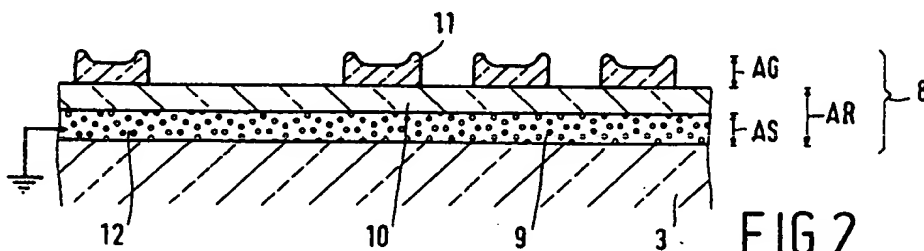
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(54) Method of manufacturing a coating on a display screen and a display device comprising a display screen having a coating.

(57) The display screen 3 of a cathode ray tube 1 is provided with an antistatic coating 8 which comprises conductive, for example ATO (Sb:SnO<sub>2</sub>) particles. The coating comprises at least one additional layer (10) of silicon dioxide to obtain an antireflective effect.

**FIG.2****EP 0 649 160 A1**

The invention relates to a method of manufacturing an antistatic coating which consists of more than one layer on a display screen and which comprises at least one antistatic layer.

The invention also relates to a display screen having an antistatic coating.

Antistatic coatings are used on display screens of display devices, in particular CRTs. Said coatings are sufficiently electroconductive to ensure that a high electrostatic voltage present on the outside surface of the display screen is removed within a few seconds. Thus, the user does not experience an unpleasant shock if he touches the screen. Besides, the attraction of atmospheric dust is reduced.

One of the layers of the coating is an antistatic layer comprising an electroconductive compound. Known coatings comprise, in addition to said antistatic layer, layers having, for example, an antireflective or antiglare effect or a layer which improves the scratch resistance. Usually said other layers are provided by spinning or spraying of a silica layer.

A method of the type mentioned in the opening paragraph is known from "Japan Display '92, pp. 289-292: "Anti-glare, Anti-reflection and antistatic (AGRAS) Coating for CRTs"", by H. Tohda et. al. In said document a method is described in which a display screen is provided with a conductive (antistatic) SnO layer by means of CVD (Chemical Vapour Deposition), whereafter a central and outermost SiO<sub>2</sub> layer are provided by, respectively, spinning, spraying and a thermal treatment.

This method is very laborious and time consuming; the CVD process is carried out in a separate reaction space. After the SnO layer is provided the surface is treated by means of polishing and cleaning.

It is an object of the invention to provide a simple method of manufacturing multilayer antistatic coatings.

In accordance with the invention, the object of providing a simple method of manufacturing a multilayer antistatic coating is achieved in that a porous layer of conductive particles is provided on the display screen, whereafter a second layer of a compound is provided and said compound penetrates into the first layer, after which said compound is converted into an additional second layer by subjecting it to a treatment at an increased temperature.

The penetrating compound causes the porous layer to be sealed and to adhere to the surface of the display screen. It is no longer necessary to subject the first layer to further treatments, such as polishing and cleaning, to obtain a satisfactory adhesion between the first and the second layer. By virtue thereof, a substantial simplification of the method is possible.

It should preferably also be possible to carry out the method at relatively low temperatures. The use of relatively low temperatures generally reduces the process time and the risk of damage as a result of thermal stresses.

To this end, an embodiment of the method in accordance with the invention is characterized in that an aqueous suspension of particles of antimony-doped tin oxide is provided on the display screen and subsequently dried thereby forming the antistatic layer, whereafter a second layer of an alcoholic alkoxy silane compound is provided on the antistatic layer, after which said alkoxy silane compound is converted into silicon dioxide by subjecting it to a treatment at an increased temperature.

This embodiment of the method in accordance with the invention enables a subsequent layer to be provided on the antistatic layer without previously curing the antistatic layer. The alkoxy silane compound can be converted into silicon dioxide at relatively low temperatures (up to 200 °C). By virtue thereof the method can be simplified.

The conversion into silicon dioxide takes place, for example, by means of a treatment of at least 30 minutes at a temperature in the range between 150 °C and 170 °C. The alkoxy groups of the alkoxy silane compound are converted into hydroxy groups by acidified water, said hydroxy groups reacting with each other and with hydroxy groups of the glass surface of the display screen. During drying and heating a firmly adhering network of silicon dioxide is formed by polycondensation.

The use of aqueous suspensions for the antimony-doped tin oxide particles has the advantage that they are less harmful to the environment. Consequently, fewer measures or perhaps no measures at all have to be taken to preclude environmental pollution, so that the method can be simplified. A further advantage is that the square resistance of the layer obtained is low, i.e. approximately 1-10 M $\Omega$ . This resistance value is much lower than the values obtained with conductive layers on the basis of ATO which are made in a different manner. A further advantage of aqueous suspensions is that the adhesion of the ATO particles to the display screen suffices to dispense with a temperature treatment after the layer has dried, so that the second layer can be directly provided, for example from an aqueous solution of an alkoxy silane compound. As soon as the coating of ATO particles has dried, the layer of the alkoxy silane solution can be provided.

The aqueous suspension is preferably provided by means of spinning. The layer thickness of the first layer, which thickness determines, *inter alia*, the optical and electrical properties of the coating, can then be accurately controlled.

The second layer is preferably provided by spinning.

By spinning of the alkoxy silane solution a homogeneous, smooth layer is formed. Optionally, a surface-active substance is added to the solution, for example in quantities of from 0.001 to 5 wt. %.

The terms "spinning" or "spin coating" generally refer to a method in which a layer is provided on a rotating member, in this case a display screen.

Preferably, both the first and the second layer are provided by spinning without interrupting the rotation of the display screen.

This has the advantage that the production of a two-layer coating can be carried out in one and the same spinning unit. The second layer can be provided without a change of position. The display screen continues to rotate, thereby precluding dust from settling on the display screen since the air flow produced above the display screen during spinning is maintained. This enables both a simplification of the method as well as an improvement of the quality of the coating.

The method in accordance with the invention can be used for applying a coating on a display screen of a display device. Within the framework of the invention it has been recognized that the preferred method can be used and, preferably, is used for applying coatings to a display screen which forms part of a cathode ray tube.

In the method disclosed in the above-mentioned article from Japan Display, a coating is applied to a display screen which constitutes a separate part, i.e. first a display screen is provided with a coating and it is not until the display screen has been provided with a coating that the cathode ray tube is assembled. This holds the risk that the coating is damaged during assembly of the cathode ray tube. This risk is avoided by providing the coating on a display screen which forms part of a cathode ray tube. The known method is not suited for this purpose.

The antistatic layer produced by means of the method in accordance with the invention comprises conductive, for example ATO (Antimony-doped Tin Oxide) particles, which ATO particles provide the antistatic properties of the layer.

Preferably, the conductive (ATO) particles used are very small, i.e. their dimensions are preferably below 50 nm. By virtue of these small dimensions no visible scattering of light occurs and the first layer formed is transparent. The particles are sufficiently electroconductive if the molar ratio Sb/Sn is smaller than 0.3.

The particle size is preferably below 30 nm. By virtue of the small dimensions of the ATO particles, Van der Waals' forces occur which cause the adhesion of the ATO particles to a glass substrate to be sufficient to provide the second layer without disturbing the first layer. The ATO particles are provided on the display screen from an aqueous, stable ATO suspension (hydrosol). In the suspension, the ATO particles are charge-stabilized instead of sterically stabilized. Such a suspension can suitably be used for the manufacture of very thin layers having a surface resistance of approximately 1-20 M $\Omega$ /square. The preparation of such an ATO suspension is described in United States Patent Specification US-A-4775412. By virtue of the small particle size, the mechanical strength of the layer suffices to directly provide a second layer without an intermediate curing step.

The first layer is preferably supplemented with layers of silicon dioxide having an antireflective or antiglare effect, said additional layers also increasing the scratch resistance. The second layer serves, *inter alia*, as an adhesive for the first layer with ATO particles. The alkoxy silane compound (for example TEOS) penetrates into the first layer and adheres to the underlying surface. Preferably, the second layer and the first layer together form a 2-layer antireflective layer. Antireflective layers are used on display screens to reduce reflection losses of traversing light and to suppress disturbing reflections in images (specular reflection). Antiglare layers are used to reduce the diffuse reflection of ambient light.

An alkoxy silane compound which can suitably be used in the method in accordance with the invention is tetraethyl orthosilicate (TEOS). It is alternatively possible to use other known alkoxy silane compounds of the type Si(OR)<sub>4</sub> and oligomers thereof, wherein R is an alkyl group, preferably a C<sub>1</sub>-C<sub>5</sub> alkyl group. For the solvent use is made of, for example, methanol or ethanol.

The invention also relates to a display device comprising a display screen having an antistatic, antireflection coating. A display device comprising a display window having an antistatic coating which consists of more than one layer and which comprises at least one antistatic layer is characterized according to the invention in that the antistatic layer is directly adjacent to the display window and comprises conductive particles having a diameter below 50 nm which are embedded in silicon dioxide, which antistatic layer is covered by a second smooth layer which contains silicon dioxide, the assembly of the first and the second layer having an antireflective effect for visible light.

The refractive index of the antistatic layer comprising conductive (ATO) particles generally differs from, and is higher than, the refractive index of the additional silicon dioxide layer. The respective layer

thicknesses of a two-layer coating are preferably selected such that destructive interference occurs at a central wavelength  $\lambda$  in the visible range, for example approximately 550 nm. For this wavelength, and for wavelengths in a range around said wavelength, the stack of layers has an antireflective effect. It is known to those skilled in the art that the optical thicknesses  $n.t$  (wherein  $n$  is the refractive index and  $t$  is the layer thickness) of the layers must be equal to  $\lambda/4$ , wherein  $\lambda$  is the central wavelength. Such an additional layer of silicon dioxide can be manufactured by providing an alcoholic solution of an alkoxy silane compound, followed by a treatment at an increased temperature, thereby forming a layer of silicon dioxide. If the additional layer is provided by spinning, the layer thickness obtained depends, *inter alia*, on the number of revolutions and the viscosity of the solution. Preferably, the particle size is smaller than 50 nm.

Preferably, a third layer of silicon dioxide having an antiglare effect is provided. This layer is provided on the first additional layer by spraying or atomizing an alcoholic solution of an alkoxy silane compound, followed by a treatment at an increased temperature, thereby forming a layer of silicon dioxide. The layer obtained is scratch resistant and has antiglare properties due to the surface texture obtained by spraying. The antiglare effect is substantially independent of the wavelength of the light. A mat surface texture is obtained by spraying or atomizing the alkoxy silane solution, so that the layer exhibits an antiglare effect. By virtue thereof, ambient light is diffusely reflected.

Further advantages of the additional layers of silicon dioxide are the reduced sensitivity to fingerprints and the higher hardness and scratch resistance.

If desired, one of the additional layers may be provided with a pigment or dye to selectively influence the light transmission. Such pigments or dyes are selected in such a manner that the light emitted by the phosphors of a cathode ray tube is selectively transmitted, whereas, for example, the ambient light reflecting at the rear side of the display screen is absorbed. Examples of pigments are transition metal oxides, such as iron oxide and chromium oxide. An example of a suitable dye is Rhodamine B.

In an embodiment of the invention, latex particles of polypyrrole are added to the aqueous solution of (ATO) particles. The polypyrrole particles provide the light-absorbing properties of the first layer. After drying, the first layer then comprises polypyrrole-latex particles.

For the polypyrrole compound use can be made of polypyrrole, N-substituted polypyrrole and  $\beta$ -substituted polypyrrole. For the substituents use can be made of: alkyl groups having, for example, up to 5 carbon atoms, aryl groups, alkoxy groups, nitro groups and halogen atoms. Such materials and the preparation of latex particles, *inter alia*, for use as an antistatic coating, are described in United States Patent Specification US-A-4959162. Also this American Patent Specification describes a centrifuging step and a re-dispersion step to purify the latex thus prepared. Preferably, the latex particles consist of unsubstituted polypyrrole.

Owing to the optical properties, uniformity and homogeneity of the layer, it is desirable for the latex particles to have uniform dimensions. The latex particles are spherical and preferably have an average diameter in the range between 50 and 150 nm. In such an embodiment, antistatic and light-absorbing properties are combined in a single layer. As a result of the method in accordance with the above embodiment of the invention, the coating comprises a homogeneous mixture of both types of particles. The layer thickness of the coating lies in the range between 50 and 200 nm. The colour of the coating is neutral grey, i.e. the transmission is independent of the wavelength. Dependent upon the layer thickness and the concentration of polypyrrole in the layer, the transmission can be adjusted, for example, between 90% and 30%, while preserving the required antistatic effect. A sufficient antistatic effect of the coating is attained if the surface resistance of the layer ranges between  $10^4$  and  $10^{10}$   $\Omega$ /square.

As described above, the combination of the coating and the additional layer of silicon dioxide exhibit an antireflective effect if the optical layer thicknesses of these layers are equal to approximately  $\lambda/4$ . The desired layer thicknesses can easily be experimentally determined. Important process parameters are the number of revolutions during spinning, the temperature and the viscosity of the solution.

The invention will be explained in greater detail by means of exemplary embodiments and with reference to a drawing, in which

Fig. 1 shows a display device,

Fig. 2 is a sectional, diagrammatic view of a display window of a display device,

Figs. 3a up to 3c show an embodiment of the method in accordance with the invention,

Fig. 4 shows the transmission  $T$  (in %) as a function of the wavelength  $\lambda$  (in nm) of a coating in accordance with the invention,

Figs. 5a and 5b show the relative reflection  $R$  (in %) as a function of the wavelength  $\lambda$  (in nm) of a coating consisting of ATO (and polypyrrole) particles carrying an additional layer of silicon dioxide and a second additional antiglare layer of silicon dioxide.

Fig. 1 is a diagrammatic cut-away view of a cathode ray tube 1 having a glass envelope 2 comprising a display screen 3, a cone 4 and a neck 5. In the neck there is provided an electron gun 6 for generating an electron beam. This electron beam is focused on a phosphor layer on the inside 7 of the display screen 3. In operation, the electron beam is deflected across the display screen 3 in two mutually perpendicular directions by means of a deflection coil system (not shown). The display screen 3 is provided on the outside with an antistatic coating 8 in accordance with the invention.

Fig. 2 is a diagrammatic, sectional view of a display screen in accordance with the invention. An antistatic coating 8 is provided on the display screen 3. Said antistatic coating 8 comprises a first layer 9 (AS), a second layer 10 and a third layer 11. The first layer 9 comprises conductive particles 12, in this case antimony-doped tin oxide particles, embedded in a second compound, in this example silicon dioxide. The second layer is made of the second-mentioned compound, in this example silicon dioxide. The first layer and the second layer together form an antireflection filter (AR). To this end, the thickness of both layers 9 and 10 is approximately  $\lambda/4$ , wherein  $\lambda$  is situated in the visible range, for example between 500 and 600 nm. The first layer may be provided with polypyrrole latex particles, enabling the transmission properties of the first layer to be determined. The third layer 11 (AG) provides an antiglare effect and consists, for example, of sprayed-on silicon dioxide.

Figs. 3a up to 3c illustrate a method in accordance with the invention.

A porous layer 31 is provided on the display screen 3. This is preferably carried out, for example, by providing an aqueous solution of conductive (ATO) particles on the display screen and drying said particles. A second layer 32 of a compound is applied to the layer 31 and said compound penetrates into the first layer. After provision of the second layer, a thermal treatment is carried out. This treatment results in the formation of a silicon dioxide layer. Subsequently, a third layer is applied to obtain an antiglare effect, for example, by spraying of a silicon-dioxide antiglare layer.

Below a description will be given of a number of embodiments of the invention.

#### Exemplary embodiment 1.

An aqueous ATO suspension is prepared as described, for example, in United States Patent Specification US-A-4775412. According to this document,  $\text{SnCl}_2$  and  $\text{SbCl}_3$  are dissolved in diluted hydrochloric acid, whereafter ammonium bicarbonate is added to the solution. In an autoclave a hydrosol of antimony-doped tin oxide is formed by hydrothermal conversion. The ATO particles are smaller than 30 nm. In a typical example, the molar ratio  $\text{Sb/Sn}$  is 0.3. The aqueous ATO suspension amounts to 5 wt. %. This ATO suspension is provided on the display screen and dried.

A solution of an alkoxy silane compound has been or is manufactured in accordance with Table 1.

Table 1: preparation of TEOS-solution (250 ml)

#### Composition and preparation:

\* mix (grams):

-TEOS	11.25
-ethanol	5.63
-0.175 M HCL	5.63

\* hydrolysing for 30 min

\* adding ethanol/butanol (1:1) to obtain 250 ml



On the first layer, which is obtained as described hereinabove (a dried layer comprising conductive particles (for example ATO)), a layer of the TEOS solution prepared in accordance with Table 1 is provided, for example, by spinning. The layer is maintained at a temperature of 160 °C for approximately 90 minutes, thereby forming a firmly adhering, smooth layer of silicon dioxide. This additional layer of silicon dioxide has a layer thickness of, for example, 135 nm and a refractive index of 1.44. This layer, in combination with the antistatic layer which comprises ATO particles and into which silicon dioxide has penetrated and which has a refractive index of 1.62 and a layer thickness of 60 nm, exhibits an antireflective effect. It is noted that the sequence in which the layers are applied is important. If the silicon dioxide layer were to be provided before the layer containing the ATO particles, this would adversely affect the adhesion of the coating and the refractive index of the layer comprising ATO particles would be different, namely approximately 1.4, and said layer would contain no or perhaps hardly any silicon oxide.

Consequently, the optical and mechanical properties of the assembly of the first and the second layer depend on the sequence in which the layers are provided. Preferably, the antistatic layer and the second layer are provided by spinning. Preferably, this is carried out in one and the same spinning unit without interrupting the spinning process of the display screen. This results in a simplification of the method and precludes dust from settling on the display screen.

Subsequently, if desired, use is made of a TEOS solution and a similar temperature treatment to provide a second additional layer of silicon dioxide by spinning. This layer has a mat surface texture having an antiglare effect. Consequently, the coating obtained is less sensitive to fingerprints. In addition, the reflection is less dependent on the wavelength because the incident light is diffusely scattered. The above method can be used to provide a coating (two-layer or multilayer) on a loose display screen, i.e. a display screen which does not (yet) form part of a cathode ray tube. Preferably, however, the method is used to provide a coating on a display screen which forms part of a cathode ray tube. The risk that the coating becomes damaged is smaller then.

#### Exemplary embodiment 2.

In this exemplary embodiment a description is given of a method and a display device in which the first layer also influences the transmission of visible light by the incorporation of polypyrrole latex particles in the first layer.

Polypyrrole latex particles are prepared by vigorously stirring a mixture of 0.938 g pyrrole, 8.65 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 1 g polyvinyl alcohol (steric stabilizer) in 100 ml water for at least 10 hours until a clear solution is obtained. The formation of polypyrrole particles can be recognized by the blackening of the mixture. The suspension obtained is dialysed with demineralised water to remove  $\text{Fe}^{2+}$  ions and  $\text{Cl}^-$  ions. After dialysis, several millilitres of ethanol, butanol and ethyl acetate are added to the suspension. Finally, the suspension is passed through a 5  $\mu\text{m}$  and a 0.2  $\mu\text{m}$  filter of polyamide. Electron microscopy shows that the latex particles have a regular, spherical shape and that they are monodisperse with an average particle size of 80 nm.

The preparation of an ATO suspension is carried out in the way described in example 1.

Equal quantities of both suspensions are subsequently mixed, thereby forming a stable suspension of ATO and polypyrrole particles. This suspension is subsequently provided on a display screen by means of spin coating. After drying, a homogeneous, neutral grey coating having a thickness of 60 nm and a resistance of 1  $\text{M}\Omega/\text{square}$  is obtained. This is amply sufficient for the desired antistatic effect (a surface resistance in the range between  $10^4$  and  $10^{10} \Omega$  is desirable) and makes it possible to bring the light transmission properties to the desired value by changing the layer thickness and the concentration of the polypyrrole, while preserving the necessary antistatic effect. The transmission T (in %) as a function of the wavelength  $\lambda$  (in nm) of the coating obtained is shown in Fig. 4. The resistance value of the coating in accordance with the invention is much lower than the values of layers of silicon dioxide in which ATO particles or polypyrrole particles with a steric stabilizer are dispersed. Such layers have a resistance of approximately 100  $\text{M}\Omega$ .

A solution of an alkoxy silane compound is prepared having the following composition: 0.9 mol tetraethyl orthosilicate (TEOS), 3.6 mol water,  $5 \cdot 10^{-4}$  mol nitric acid, which is made up to 1 litre by adding ethanol.

The first layer obtained in accordance with exemplary embodiment 2 is provided with a layer of said TEOS solution by spinning. The layer is maintained at a temperature of 160 °C for 30 minutes, thereby forming a firmly adhering, smooth layer of silicon dioxide. This additional layer of silicon dioxide has a layer thickness of 135 nm and a refractive index of 1.44. This layer, in combination with the coating which comprises ATO and polypyrrole particles and which has a refractive index of 1.62 and a layer thickness of 60 nm, has an antireflective effect.

Subsequently, the same TEOS solution is used and a similar temperature treatment is carried out to provide a second additional layer of silicon dioxide by spraying. This layer has a mat surface texture having an antiglare effect. As a result, the coating obtained is less sensitive to fingerprints. In addition, the reflection is less dependent on the wavelength because the incident light is diffusely scattered.

Fig. 5a represents the relative reflection R (in %) as a function of the wavelength  $\lambda$  (in nm) of a coating consisting of the above-described layer of ATO particles (example 1) on which the additional layer of silicon dioxide and an antiglare layer (curve A) are provided. In the measuring process, uncoated display-screen glass is used as the reference material.

Fig. 5b represents the relative reflection R (in %) as a function of the wavelength  $\lambda$  (in nm) of a coating consisting of the above-described layer of ATO and polypyrrole particles (example 2) on which the additional layer of silicon dioxide (curve A) is provided. In the measuring process, uncoated displayscreen glass is used as the reference material. Curve B shows the effect of the additional antiglare layer. The antireflective effect of the coating has become less dependent on the wavelength.

The scratch resistance of the outermost layer is tested by means of a conical diamond which is moved over the surface at a force of 50 g and which does not form scratches which are visible to the naked eye.

The hardness is tested by means of a pencil-hardness test in which pencils having a different hardness exert a force of 7.5 N on the surface over which they are moved at an angle of 45° and a velocity of 0.05 m/s. In accordance with this test, the inventive layer has a degree of hardness of from 3 H to 4 H.

By means of the invention, effective antistatic coatings and, if desired, light-absorbing coatings are manufactured and provided on a display screen of a cathode ray tube in a simple manner, said coatings enabling the light-transmission properties to be adjusted, whether or not as a function of the wavelength.

## Claims

1. A method of manufacturing an antistatic coating which consists of more than one layer on a display screen and which comprises at least one antistatic layer, characterized in that a porous layer of conductive particles is provided, whereafter a second layer of a compound is provided and said compound penetrates into the first layer, after which said compound is converted into an additional second layer by subjecting it to a treatment at an increased temperature.
2. A method of manufacturing an antistatic coating which consists of more than one layer on a display screen and which comprises at least one antistatic layer, characterized in that an aqueous suspension of conductive particles of antimony-doped tin oxide is provided on the display screen and subsequently dried, thereby forming the antistatic layer, whereafter a second layer of an alcoholic alkoxy silane compound is provided, after which said alkoxy silane compound is converted into silicon dioxide by subjecting it to a treatment at an increased temperature.
3. A method as claimed in Claim 2, characterized in that the aqueous suspension is provided by means of spinning.
4. A method as claimed in Claim 1 or 2, characterized in that the second layer is provided by means of spinning.
5. A method as claimed in Claims 2 and 3, characterized in that the first and the second layer are provided by spinning without interrupting the rotation of the display screen.
6. A method as claimed in Claim 1, 2, 3 or 4, characterized in that the antistatic coating is provided on a display screen which forms part of a cathode ray tube.
7. A method as claimed in any one of the preceding Claims, characterized in that the conductive particles are smaller than 50 nm.
8. A method as claimed in Claim 1, 2, 3, 5 or 6, characterized in that the conductive particles are smaller than 30 nm.
9. A method as claimed in Claim 2, 3, 4, 5 or 7, characterized in that latex particles of polypyrrole are added to the aqueous solution of ATO particles.

10. A method as claimed in any one of the preceding Claims, characterized in that a third layer of an alcoholic solution of an alkoxy silane compound is sprayed onto the second layer, whereafter the alkoxy silane compound is converted into a further additional layer of silicon dioxide by subjecting it to a treatment at an increased temperature, said further additional layer producing an antiglare effect.
11. A method as claimed in any one of the preceding Claims, characterized in that the first layer and the additional layer together produce an antireflective effect.
12. A display device comprising a display window having an antistatic coating which consists of more than one layer and which comprises at least one antistatic layer, characterized in that the antistatic layer is directly adjacent to the display window and comprises conductive particles having a diameter below 50 nm which are embedded in silicon dioxide, which antistatic layer is covered by a second smooth layer which contains silicon dioxide, the assembly of the first and the second layer having an antireflective effect for visible light.
13. A display device as claimed in Claim 11, characterized in that the conductive particles contain antimony-doped tin oxide (ATO).
14. A display device as claimed in Claim 11 or 12, characterized in that the antistatic layer and the second layer each have an optical thickness of  $\lambda/4$ ,  $\lambda$  being a wavelength situated in the visible range.
15. A display device as claimed in Claim 11, 12 or 13, characterized in that a third layer of silicon dioxide having an antiglare effect is provided on the second layer.
16. A display device as claimed in Claim 11, 12, 13 or 14, characterized in that at least one of the additional layers is provided with a pigment or dye to selectively influence the light transmission.
17. A display device as claimed in Claim 11, 12, 13, 14 or 15, characterized in that the first layer comprises polypyrrole latex particles.
18. A display device as claimed in Claim 15, characterized in that the latex particles have an average diameter in the range between 50 and 150 nm.
19. A display device as claimed in Claim 12 or 13, characterized in that the coating has a surface resistance in the range between 1 and 20 M $\Omega$ /square.

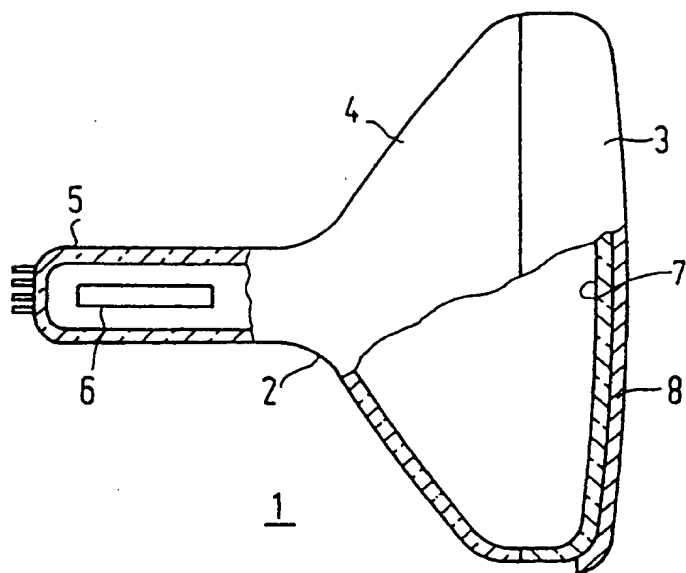


FIG. 1

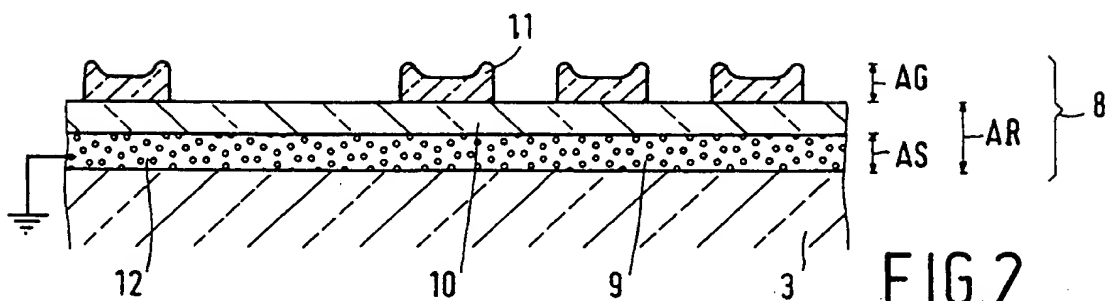


FIG. 2

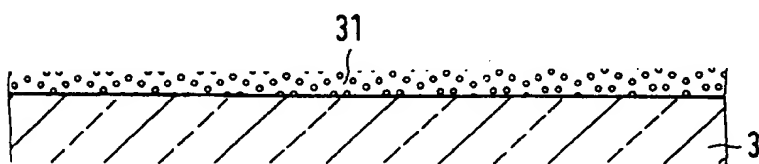


FIG. 3A

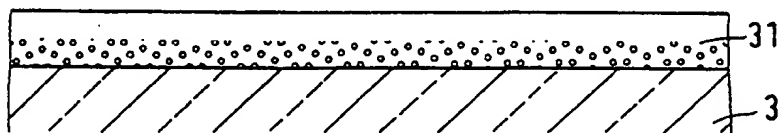


FIG. 3B

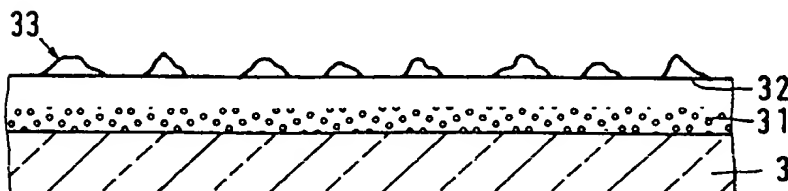
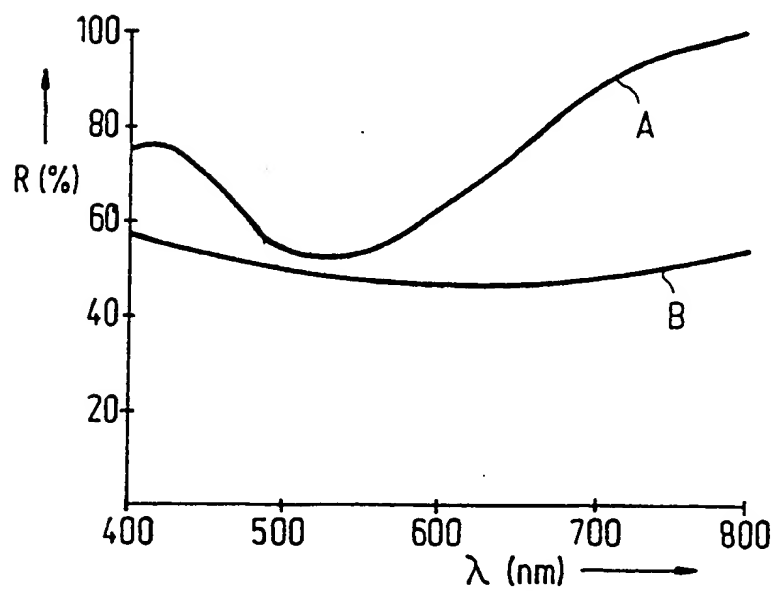
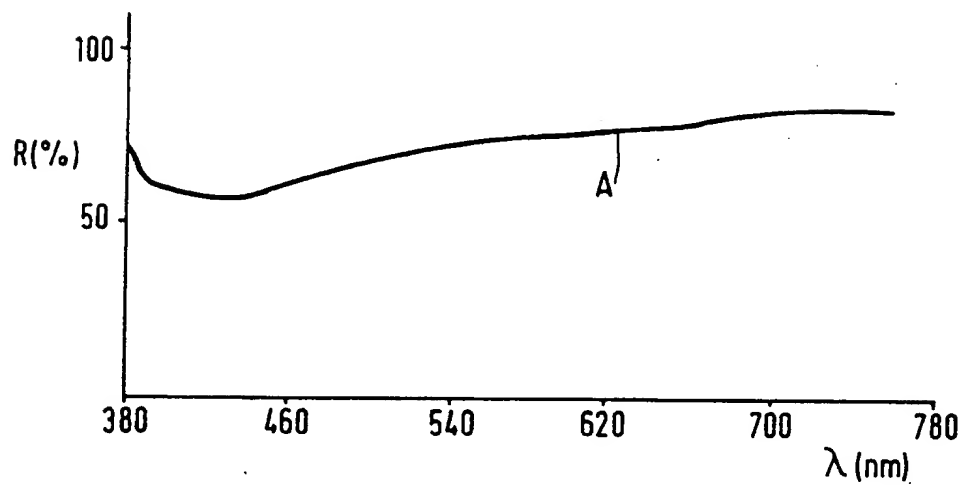
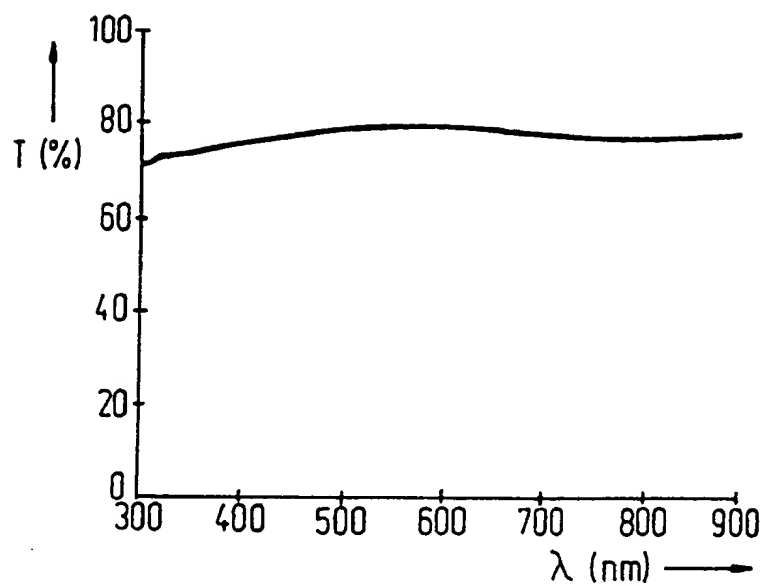


FIG. 3C





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## EUROPEAN SEARCH REPORT

Application Number  
EP 94 20 2991

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP-A-0 538 937 (PHILIPS) * samenvatting * * column 5, line 44 - column 6, line 49 * ---	1-7,12, 13,16	H01J29/86 H01J9/20
D,A	EP-A-0 533 256 (PHILIPS) * column 3, line 23 - column 4, line 11 * ---	1,2,9	
A	EP-A-0 552 796 (ASAHI GLASS) * claims 1-6 * ---	1	
A	US-A-5 150 004 (H.S.TONG ET AL.) * samenvatting * * column 1, line 44 - line 56 * ---	1,2	
A	DE-A-39 32 343 (MITSUBISHI) * samenvatting * * claims 1-13 * -----	1,3	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01J C03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 25 January 1995	Examiner Daman, M
CATEGORY OF CITED DOCUMENTS			
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